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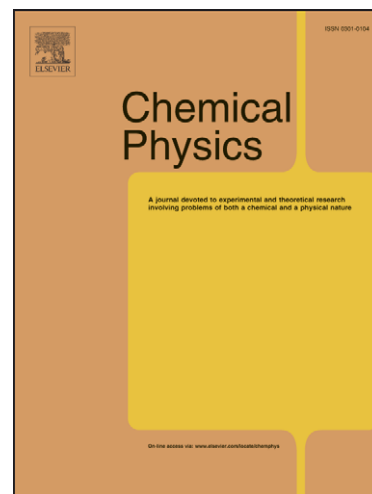
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Threshold photoelectron studies of isoxazole over the energy range 9.9-30 eV

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Abstract

The threshold photoelectron spectrum of the isoxazole molecule, C₃H₃NO has been measured over the photon energy range 9.9eV to 30eV with the use of synchrotron radiation. In the 9.9-10.8 eV range, corresponding to photoionization from the highest occupied molecular orbital 3a''(π), seven well resolved vibrational series have been observed and their modes are tentatively assigned. A strong adiabatic ionization, with an energy of 11.132 ± 0.003 eV corresponding to the 2a''(π) band, has also been observed. This is followed by a single vibrational series of the ν_{C-H} stretching mode. Photoelectron bands in the energy region 13-30 eV have also been identified, some for the first time.

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Keywords: isoxazole; photoelectron spectroscopy; threshold photoionization

1. Introduction

Ionizing radiation can produce a range of structural and chemical modifications of the DNA double helix. In particular, double-strand breaks, where both strands of the helix are broken within a few base pairs, can lead to lasting damage via the production of chromosome aberrations, i. e. mutations that ultimately lead to killing of the cell. The effectiveness of ionizing radiation to induce damage is critically dependent on the pattern of the ionization produced on a nanometer scale, i. e. on a scale comparable to the dimensions of the DNA helix. Theoretical modeling of track structure is therefore being used to simulate the distinctive patterns of ionization produced by a wide range of ionizing radiation to characterize the mechanisms by which different types of radiation damage DNA [1]. Valuable information on energy deposition by ionizing radiation may be obtained by exploring the photoionization of the component molecules of DNA and other cellular macromolecules since such processes yield low-energy photoelectrons. These photoelectrons may produce damage to DNA via dissociative electron attachment taking place close to the ionization site. In contrast to our knowledge of the mechanisms of electron induced damage, our information on the site selective molecular damage in DNA induced by photon impact is limited .

Some heterocyclic molecules, which are based on the five-membered aromatic ring containing one or two heteroatoms (oxygen and nitrogen atoms), may be used as simple analogues of building blocks of DNA, the nucleotides. Hence they may be used to

explore the effects of ionizing radiation on DNA. These heterocyclic molecules play also an important role in many pharmaceutical and agricultural applications such as the synthesis of antibiotics, antitumour, anti-HIV and herbicidal agents [1]. Isoxazole is a five-membered heterocycle molecule (Fig. 1) belonging to the C_s point group and is related to furan (C_{2v} point group) by replacing the CH group in the furan ring with an N atom at position 2. The effect of introducing the N atom into the furan ring results in a shortening of the 2-3 distance between the nitrogen and carbon atoms in the double bond and an increase in the C_3 bond angle [2,3]. These changes in the geometrical parameters affect the energies of the molecular orbitals, lower the vertical attachment energies (unoccupied orbitals) [2] and increase the ionization energies (occupied orbitals) in isoxazole as compared to furan [3]. Both isoxazole and furan have a fully conjugated set of π electrons with the two highest occupied orbitals being π_2 and π_3 . The complete set of the occupied molecular orbitals of the X^1A' ground state of isoxazole is $1...14(a')^2 15(a')^2 1(a'')^2 2(a'')^2 3(a'')^2$. The $15(a')^2$ orbital is the σ nitrogen lone pair (LP_N)² and the $1a''$, $2a''$ and $3a''$ orbitals are labeled π_1 , π_2 and π_3 , respectively. Ionization energies of the orbitals of isoxazole have been calculated using the Hartree-Fock method [4,5] and more recently by the configuration interaction (CI) method with the inclusion of Green's Function and Tamm-Dancoff non-diagonal approximations [3].

The isoxazole molecule is a planar near oblate asymmetric top possessing 18 normal vibrational modes which all are infrared active. The vibrational modes and structural properties of the neutral isoxazole (and isoxazole- d_3) molecules have been determined from measurements of Raman and IR spectra in the vapour phase [6-9], aided by extensive theoretical calculations [8,10-12]. In the most recent calculations [11,12], the IR and Raman spectra of isoxazole and isoxazole- d_3 have been reassigned with the aid of DFT theory [11] and a systematic study of the anharmonic vibrational frequencies

has been carried out using both the B3LYP density functional and MP2 ab initio techniques [12]. The totally symmetric $\nu_1(A')\text{-}\nu_{13}(A')$ modes are the in-plane vibrations while the $\nu_{14}(A'')\text{-}\nu_{18}(A'')$ are out-of plane vibrations. The energies of the three C-H stretching modes $\nu_1\text{-}\nu_3$ are located near 3300 cm^{-1} (409 meV) and the energies of the remaining modes lie below 1700 cm^{-1} (211 meV).

Although the furan molecule has been extensively investigated in photoelectron studies, see e. g. [13] and references therein, analogous investigations in isoxazole are rather scarce. The He(I) photoelectron spectra of isoxazole have been measured by Palmer et al. [4], Baker et al [14] and Kobayashi et al. [15]. In the last work [15], photoelectron angular distributions were also measured and compared with the first-order calculations. More recently Walker et al. [3] presented the He(I) photoelectron spectra obtained with an improved resolution of 20 meV.

In this paper we report high-resolution, threshold photoelectron spectra of isoxazole, obtained with the use of synchrotron radiation in the photon energy range 9.9 - 30 eV. These results significantly extend earlier He(I) photoionization measurements both by the energy range studied and the number of vibrational series that are revealed in the ionization bands. The high energy resolution of the measurements (12 meV) has enabled the ionization band of the highest occupied molecular orbital $3a''(\pi)$ to be resolved into seven series of vibrational structures. These present measurements were made in the regime of threshold ionization where the ejected photoelectrons have near-zero energy. Hence, the observed intensities of the spectral features give relative yields of these near-zero energy electrons produced by the various ionic states of the isoxazole molecule. Knowing the sources and abundances of such electrons may help in assessing the scale of damage in the DNA helix induced by secondary electrons.

2. Experimental details

The threshold photoelectron spectra presented in this paper were recorded at the Daresbury Synchrotron Radiation Source, UK. The experimental setup and the methodology are identical to those applied in our recent measurements of the threshold photoelectron spectrum of tetrahydrofuran [16]. Briefly, radiation from the McPherson 5-m normal incidence monochromator entered the interaction region, via a pyrex capillary tube with an internal diameter of 1 mm. The photon bandpass was 0.5 Å. The photon flux was monitored with an aluminium oxide photodiode whose signal was used to normalize the measured spectra with respect to incident photon flux.

Threshold photoelectron spectra were recorded by a photoelectron spectrometer employing the penetrating field technique [17], which has been described in detail previously [18]. The penetrating electrostatic field collects photoelectrons having energies lower than about 5 meV with very high efficiency and simultaneously discriminates against higher energy photoelectrons. The performance of the spectrometer was optimized by recording the $^2P_{3/2}$ (15.760 eV) and $^2P_{1/2}$ (15.937 eV) ionic lines of argon. The observed ratio of their intensities (6:1) indicated that threshold electrons with energies of less than 5 meV were being detected [17]. The photon energy scale was calibrated to within ± 3 meV against ionic lines of the rare gases. The overall energy resolution of the present measurements in the low energy region was 12 meV but increased to about 30 meV at 25 eV. The overall resolution results from a combination of the photon bandpass and the threshold resolution of the spectrometer. The energy resolution of 12 meV results from the 4 meV photon energy spread and 8 meV resolution of the threshold spectrometer.

The isoxazole molecular beam at the interaction region was formed by a 0.6 mm inner diameter capillary. Isoxazole is a liquid at room temperature with a vapour pressure of about 0.3 bar. This allowed the use of a needle valve to set an optimum

target density in the interaction region. The background pressure in the experimental chamber was typically 2×10^{-5} mbar while the estimated pressure in the interaction region was approximately 60 times higher. The isoxazole sample, obtained from Sigma-Aldrich Company Ltd with a stated purity of 99%, was degassed several times in the sample container to remove any contaminating gases before introducing it through the gas line into the interaction region.

3. Results and discussion

The complete threshold photoelectron spectrum of isoxazole obtained in the present study, over the energy range 9.9-30 eV, is displayed in Fig. 2. It consists of six distinct groups of ionization bands of which the three highest intensity bands are positioned in the energy intervals 9.9-10.8, 10.8-13 and 13-16.7 eV. The photoelectron count rate for the peak at 14.5 eV was equal to 4 kHz under typical conditions of gas pressure and photon flux. The energy width of the photon beam in the spectrum of Fig.2, at a fixed bandpass of 0.5 Å varied across the spectrum from 4 meV at 10 eV to 25 meV at 25 eV. The energy range covered in this work extends beyond 20 eV, higher than in previous measurements [4,14] .

Fig. 3 shows the first photoelectron band, which corresponds to ionization from the highest occupied molecular orbital $3a''(\pi)$ [4,15]. This band shows multiple vibrational lines superimposed on a broad peak having a maximum at 10.33 eV. Due to the improved energy resolution (12 meV) of the present measurements compared to previous He(I) studies [3] (20 meV), more vibrational peaks have been resolved. To aid the identification of the observed vibrational series, the smoothly varying intensity of the broad peak, shown in Fig. 3 by a dashed line has been subtracted from the original spectrum. The resultant vibrational intensities, displayed in the inset of Fig. 3, enabled

differentiation of seven vibrational series of the $3a''(\pi) {}^2A''$ ionic state. The energy of the 0-0 transition, corresponding to the adiabatic ionization transition, is determined to be 9.976 eV. This value is in good agreement with that obtained earlier in the measurements of the He(I) spectrum [14]. The strong 0-0 transition is followed by five resolved vibrational series (Fig. 3). For four of these series the first excited vibrational levels have a much lower intensity than the 0-0 adiabatic transition. Moreover, they have very short vibrational progressions (one or two excited vibrational levels). These features indicate that there is little change during ionization in the potential energy surface which generates these vibrational series and furthermore that the vibrational energies of the ion are similar to the corresponding energies of the ground state of the neutral molecule. The fifth series has a longer vibrational progression, indicating that the vibrational energy of the mode may be more different to that of the ground state. We discern four of its excited vibrational members.

To assign, at least tentatively, the modes corresponding to the above ionic vibrational series, we have compared our determined vibrational energies with those of the isoxazole ground state taking into account the above considerations. We suggest tentatively the following vibrational modes for the observed series, with their vibrational energies given in parentheses: ν_{18} or ν_{17} (68 meV), ν_{16} (99 meV), ν_7 (147 meV), ν_6 (171 meV) and ν_5 (181 meV). The vibrational energy (68 meV) of the longer series tentatively assigned to ν_{18} or ν_{17} is lower than that of the neutral ground state by 5 and 10 meV, respectively. The differences in the remaining series are not more than 4 meV. In the spectrum of Fig. 3 we also identify two combination series, namely, $\nu_6 + \nu_{18(17)}$ (235 meV) and $\nu_5 + \nu_{18(17)}$ (247 meV). A very low intensity peak is observed at 9.949 eV, which is 27 meV below the 0-0 transition. Its energy position precludes its assignment to a hot band as the lowest vibrational energy of the ground state is 73 meV

(ν_{18}). This structure may be due to the production of very low energy electrons by highly excited Rydberg states. Such signals have been seen previously in threshold photoionization studies, for example in argon [18].

The energies of the resolved peaks observed in the threshold photoelectron spectrum of isoxazole are listed in Table 1 and were obtained using a fitting program. These are given together with the proposed, tentative assignments of the vibrational modes. In the threshold photoelectron spectrum of the related molecule furan [19], the first ionization band X^2A_2 , displays similar characteristics, i. e. short vibrational series and energies corresponding to that of the ground state. However, in the furan spectrum these vibrational series are not superimposed on a broad peak as is observed for isoxazole in the present work. This difference may be due to the differences in the potential energy surfaces of the ground ionic states of these two molecules. This broad peak in isoxazole is not generated by overlapping, unresolved vibrational progressions.

The threshold photoelectron spectrum of isoxazole obtained in the energy range 10.8-12.8 eV is shown in Fig. 4 and covers the regions of the $2a''(\pi)$ and $15a'(LP_n)$ bands. These assignments were proposed by Palmer et al. [14] on the basis of ab initio calculations and verified by measurements of β -asymmetry parameters by Kobayashi et al. [15]. The spectrum shows an underlying broad feature and superimposed upon the rising slope of this broad feature, there is a sharply rising threshold peak which is followed at higher energies by additional structures. The broad feature is approximated by a dashed line in Fig. 4. To show more clearly the sharp structures, we have subtracted the broad band from the original spectrum and the result is shown in the inset of Fig. 4. We assign the sharp threshold peak at 11.132 eV, together with the associated structures extending over about 0.5 eV, to the $2a''(\pi)$ ionization band while the broad

band with a maximum at 11.4 eV is assigned to the $15a'(LP_n)$ band. We can discern a single vibrational series attributed to the C-H stretching mode in the $2a''(\pi)$ band. Our interpretation of the $2a''(\pi)$ band is supported by comparison with the second $(\pi) A^2A_2$ band of furan. The two narrow structures seen at 11.690 and 12.615 eV and the variation of the intensity between the structures (Fig. 4a) are most likely due to the broad $15a'(LP_n)$ band. The energies of the structures resolved in the bands of Fig. 4 are listed in Table 2.

The threshold photoelectron spectra of isoxazole obtained in the energy region above 13eV are shown in Fig.5. This region contains several ionization bands of the isoxazole molecule, some of which are observed for the first time in the present study. To resolve the band structures more clearly, the photoelectron spectra have been fitted by a number of Gaussian functions. A good fit to the overall spectra has been obtained, as is shown in Fig. 5, supporting the use of Gaussians as a reasonable approximation to the band shapes. Some of the revealed bands have higher widths and may be composed of several narrower features. In the fitting procedure, we have assumed the height of the background to change smoothly from 13 eV to 22 eV, as is indicated by a dashed curve in Fig. 5. The determined energies of the bands are given in Table 3 together with those obtained from the He(I) photoelectron spectra [4,14]. The uncertainty in the energies obtained from the fitting is estimated to be 30 meV. The table also gives the results of CI calculations [3] and the assignments of the bands. The broad feature between 13 eV and 16.5 eV is well fitted by five bands. Although the wider band at 15.42 eV is not seen directly in the spectrum, its presence is confirmed by the good fit to the experimental spectrum in this region. The bands at 13.74eV, 14.49eV and 15.58eV are assigned to the $14a'$, $13a'$ and $12a'$ states, respectively following the CI calculations of Walker et al [3]. The remaining two bands may be assigned to the $1a''(\pi)$ state and/or

shake-up states with leading terms of $1a''(\pi)$ and $11a'$, which are predicted in this energy range by calculations [3]. The next two bands that are resolved in the fitting procedure, at 17.51 eV and 17.88 eV, are assigned tentatively to $1a''(\pi)-\pi^*\pi\pi$ and $11a'-\pi^*\pi15a'$ shake-up states, respectively, following the CI calculations [3]. The broad feature at 19.5 eV is fitted well by two bands centered at 19.01 eV and 19.81 eV albeit with very different intensities. These most likely correspond to the $10a'$ and $9a'$ orbitals [3]. Above 22 eV we detect three weak bands at 22.95, 24.49 and 26.44 eV. No assignment for these bands has been attempted and it is worth pointing that at these energies the single particle model for ionization becomes invalid.

4. Conclusions

We present results of a threshold photoionization study of the isoxazole molecule using synchrotron radiation. Threshold photoelectron spectra have been recorded with a resolution as high as 12 meV. In the energy range 9.9-10.8 eV, corresponding to the highest occupied $3a''(\pi)$ molecular orbital, the progressions of seven vibrational modes have been detected and tentatively assigned. The $3a''(\pi)$ adiabatic ionization energy has been determined to be 9.976 ± 0.003 eV. The shape of $2a''(\pi)$ band has been determined in the range of 0.5 eV above its adiabatic ionization energy and a single vibrational series of the ν_{C-H} stretching mode has been identified. The $2a''(\pi)$ adiabatic ionization energy has been found to be 11.132 ± 0.003 eV. In the energy region 13-30 eV a number of ionization bands has been revealed, some for the first time. The assignments of some of these bands have been suggested from comparison with CI theoretical calculations.

Acknowledgements

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Table 1. Energies and tentative assignments of the vibrational peaks observed in the threshold photoelectron spectrum of the $3a''(\pi)$ band of isoxazole.

Binding energy (eV)	Assignment	Vibrational energy (meV)
9.949		
9.976	0-0	0
10.044	$\nu_{18(17)}$	68
10.075	ν_{16}	99
10.107	$2\nu_{18(17)}$	131
10.123	ν_7	147
10.147	ν_6	171
10.157	ν_5	181
10.171	$3\nu_{18(17)}$	195
10.188		212
10.211	$\nu_6+\nu_{18(17)}$	235
10.223	$\nu_5+\nu_{18(17)}$	247
10.235	$4\nu_{18(17)}$	259
10.255		279
10.271	$\nu_6+2\nu_{18(17)}$	295
10.283	$\nu_5+2\nu_{18(17)}$	307
10.301		325
10.321	$2\nu_6$	345
10.331	$\nu_6+3\nu_{18(17)}$	355

Table 2. Energies and tentative assignments of structures observed in the threshold photoelectron spectrum of the $2a''(\pi)$ and $15a'(LP_n)$ bands of isoxazole.

Energy (eV)	Assignment	Vibrational energy (meV)
11.132	0-0	0
11.28		
11.460	ν_{C-H}	328
11.690		
11.79	$2\nu_{C-H}$	658
11.95		
12.2		
12.35		
12.615		

Table 3. Measured and calculated vertical ionization energies (in eV) and assignments of the bands observed in photoelectron spectra of isoxazole in the photon energy range above 13 eV.

Present work TPES	Baker et al. [14] PES	Palmer et al. [4] PES	Walker et al. [3] CI	Assignment
13.74	13.85	13.83	13.755	14a'
14.49	14.61	14.55	14.546	13a'
15.42				
15.58	15.64	15.60	15.614	12a'
15.87				
17.51			17.312	1a''(π)- π^*_π
17.88	17.81	17.75	17.940	11a'- π^*_π 15a'
19.01		18.50		10a'
19.81				9a'
22.95				
24.49				
26.44				

Figure captions

Fig. 1. Schematic diagram of the isoxazole molecule C_3H_3NO showing numbering of the atoms. Color code: the carbon atom is gray, oxygen atom red, nitrogen atom light blue, hydrogen atom dark blue.

Fig. 2. An overall threshold photoelectron spectrum of isoxazole measured over the photon energy range 9.9-30 eV.

Fig. 3. Threshold photoelectron spectrum of isoxazole measured over the photon energy range corresponding to ionization from the 3a''(π) orbital. (a) The inset displays the difference between the original spectrum of the main figure and a broad peak shown by a dashed line.

Fig. 4. Threshold photoelectron spectrum of isoxazole measured over the photon energy range corresponding to ionization from the 3a''(π) and 15a'(LP_n) orbitals. (a) The inset displays the difference between the original spectrum of the main figure and the broad peak shown by a dashed line.

Fig. 5. Threshold photoelectron spectrum of isoxazole measured over the photon energy range 12.5-30 eV. Also shown, as dashed lines, are the bands fitted to the experimental spectrum and a smoothly varying background. The solid (red) line is the final fit of the spectrum.

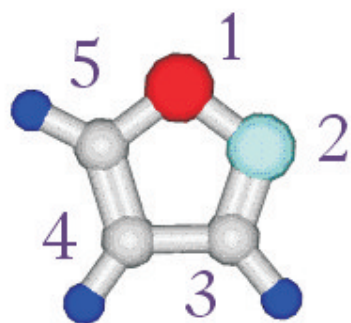


Fig1

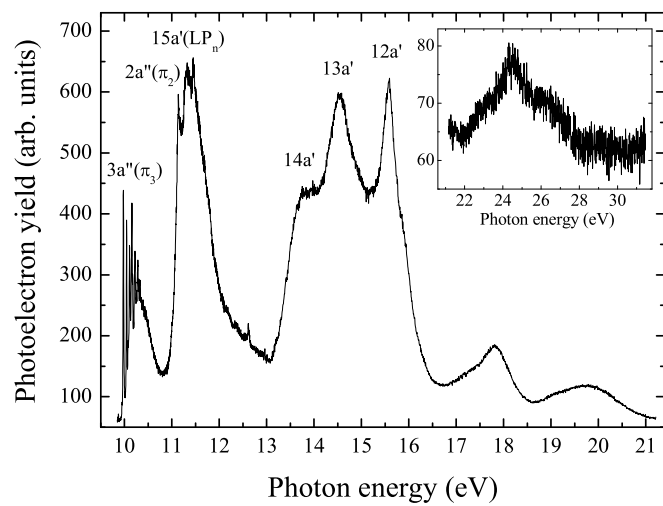


Fig2

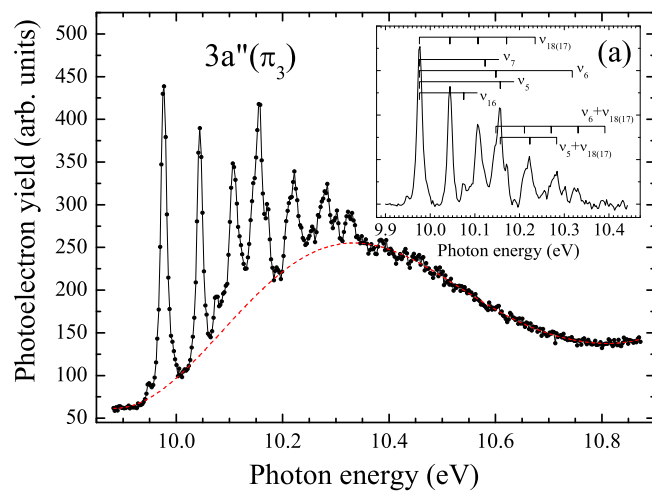


Fig3

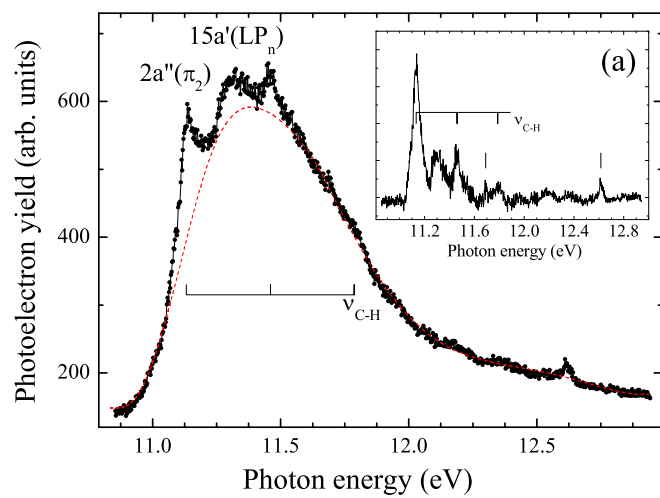


Fig4

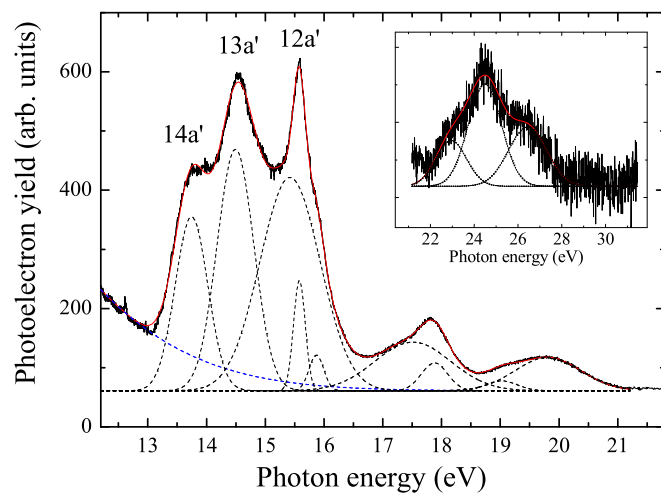


Fig5

Binding energy (eV)	Assignment	Vibrational energy (meV)
9.949		
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Table1

Binding energy (eV)	Assignment	Vibrational energy (meV)
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Table2

Present work TPES	Baker et al. [14] PES	Palmer et al. [4] PES	Walker et al. [3] CI	Assignment
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14.49	14.61	14.55	14.546	13a'
15.42				
15.58	15.64	15.60	15.614	12a'
15.87				
17.51			17.312	1a''(π_1)- $\pi_4^*\pi_3\pi_2$
17.88	17.81	17.75	17.940	11a' - $\pi_4^*\pi_5$ 15a'
19.01		18.50		10a'
19.81				9a'
22.95				
24.49				
26.44				

Table3